

PREPARATION AND STRUCTURE CHARACTERIZATION OF PHENOLIC POLYMER BY TGA METHOD

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ABSTRACT

The synthesis linear p- Substituted polymer at different temperature i.e. 120 °C for 6 hours and at 150 °C for 12 hours. Analysis by thermal gravimetric analysis method (TGA), calculated thermal activation energy (E_a) and thermal degradation at different Temperature with mass loss in percentage, calculate theoretically mass loss, thermal stability, we have studied the structure analysis. From TGA with respect to mass loss at different temperature. These polymers possessed high molecular weight low proportion of unreached methylene groups. With these sample of polymers were analysed/ characterization by TGA method excellently.

KEYWORDS: TGA, TG, Phenol, Methylene, Activation Energy, Thermal Degradation, Stability

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INTRODUCTION

The condensation of phenol with acetaldehyde in presence of acid catalyst gave resinous products reported by Beayar¹. Manasse² independently synthesised ortho-hydroxybenzyl alcohol by low temperature alkaline – catalyzed formaldehyde reaction. Other³⁻⁶ also prepared interesting compounds from phenol and formaldehyde. Beakeland, ⁷ granted a patent in 1909, describing his alkaline catalyzed Bakelite resins and also acid –catalyzed novalac product. Since then owing to their exceptional stability and other useful properties, these resins continue to find widespread uses. The reaction has been generally accepted that the phenol and alcohol condense with the elimination of water to yield three-dimensional macromolecules cross linked by methylene bridges.⁸

Thermal stability of the polymer is highly dependent on the nature of the monomer unit, the structure of the polymer chain and reactivity of the macromolecule from the analysis the different polymers. It is revealed that the presence of rings in the backbone enhance the rigidity and her raises the melting points⁹. Introduction to double bonds into a player molecule increases its flexibility. On the other hand the presence of conjugated double, triple bonds and cross linking makes the molecules more rigid and raises the softening point. The intermolecular forces are responsible for the mechanical strength of the polymer and also for the thermal stability. Evolutionary modification of the known polymer systems, discovery of the new families of polymers by imaginative synthesis and greater understanding of structure property relations in polymer continually serve to enlarge the horizons of plastic materials¹⁰.

Polymeric ablators can be categorized into two types, such as are subliming ablators and charring ablators. Ideal subliming ablators are those which undergo thermal depolymerisation quantitatively and reversibility. But on the other hand, the most important feature of charring ablators for service under hyper thermal condition is that they must undergo cross linking reactions on pyrolysis and generate a dense carbonaceous char in high yield.

The polymer scientists are now trying to synthesis phenol formaldehyde polymers which encompass both high

temperature stability and capacity to have prominent place in all branches of science and technology. It is more different to determine the content of aromatic carbons in different substitution patterns.¹⁰ on the depending molar ratio of phenol to formaldehyde and catalyst can be obtained different resin structures.¹¹

Phenolic resin is increasingly used in building structural materials due to its good thermal isolation, high dimensional stability and particularly outstanding flame retardant properties.¹²⁻¹⁵ Phenol formaldehyde resin application have severely restricted by its high brittleness and pulverisation, which is related to the lack of flexible functional groups in its chemical structures.¹⁶⁻¹⁷ considering the high price of modifiers from renewable natural compounds like tannin¹⁸ have been a focus of research in recent years.

EXPERIMENTAL

Preparation of Polymer¹⁹

0.01 mole of p –chloro phenol was dissolved in 10.0 mol NaOH solution and 0.02 mol of formaldehyde (37 % solution) was added while stirring. To this homogenous mixture, 0.01 mol of p – substituted benzoic acid (p – chloro, p – nitro) was added and deaerated by passing N₂ gas, The mixture was refluxed at 120° C - 150° C for 6 - 12 Hrs. On acidification a solid mass was obtained and dried. This dried coloured was used in studies.

Method for Thermal Gravimetric Analysis

The automatic recording thermogravimetric analysis in N₂ atmosphere was carried at RSIC, Nagpur University, Nagpur on Perkin – Elmer. Thermal analysis system TGS₂ thermal analysis in temperature range 40-900°C with heating rate 10°C /min.

Thermogravimetric is the method in which the mass of the sample is continuously recorded during heating. The thermo gravimetric curve thus obtained expressing the dependence of the mass change on temperature gives information of the sample composition. Its thermal stability, its thermal decomposition, the product formed on heating and kinetic parameters.

A number of method have been proposed for estimating kinetic parameters from dynamic TGA studies.²⁰⁻²¹ Shape-Wentworth method²² is used to determine above mentioned parameter. In the following reaction,



Where, X & Y are solid and Z could be a volatile or gaseous product. The rate of disappearance of x may be expressed as,

$$dc/dt=k(1-c)^n \quad (2)$$

is

below,

$$k = A e^{-E_a/RT} \quad (3)$$

For a linear heating rate, β in deg/min;

$$\beta = dT/dt \quad (4)$$

$$\text{or } dt = \beta \, dc$$

$$dc/dt = \beta \, dc/dt \quad (5)$$

from equation (2) & (5), we get equation (6) by putting value of R from equation (3), become as

$$\beta (dc/dt) = A e^{-E_a/RT} (1-C)^n \quad (6)$$

On arrangement, we get

$$(dc/dt) / (1-c)^n = (A/\beta) e^{-E_a/RT} \quad (7)$$

taking logarithm on both sides, the equation becomes

$$\log [(dc/dt) / (1-c)^n] = \log (A/\beta) - (E_a/2.303 RT) \quad (8)$$

If $n=1$, then the reaction having first order the equation (8) reduces to

$$\log [(dc/dt)/(1-c)] = \log(A/\beta) - (E_a/2.303 RT) \quad (9)$$

If we apply the equation (9) to simple TG curve, total mass loss at the end is taken as the active mass a_0 of the substance participating in the degradation process and this value. a_0 is taken into account. While calculating functional mass loss (c) at given temperature but the situation is somewhat different in a two stage degradation reaction. Here these two steps are theoretically separated from each other by using a method adopted by Papazian²³ and each step is individually analysed for evaluation of kinetic parameter by using sharp Wentworth method. In present investigation the degradation has been observed to follow a single sigmoidal path. Therefore equation (9) can be applied to it.

RESULTS AND DISCUSSION

The infra red spectral peaks are analysed as shown in Table 1. Which are assign at different wavelength with respect to bonds.

TGA is seen that the stability of the polymer depends on the p- substituted group on phenol from table.2 TG curves are indicates that the thermal stability of strained chain polymers is less than flat or linear chain polymers such as different high polymerisation temperature TG thermogram of poly (4- chlorophenol – methylene- -4- chlorobenzoic acid) in nitrogen atmosphere is shown in Figure.1.

From these figures it is noted that in nitrogen atmosphere, the sample which refluxed at 150°C for 12 hours is more thermally stable than the sample prepared at 120°C for 6 hours. During product formation the moisture will be trapped due to these water molecules the mass loss occurs at around 120-130°C temperature.

The degradation temperature is noted in Table 2. The continuous degradation of the pure sample. The most important step is post curing and oxidation degradation in temperature range 250-400°C. The mass loss due to products formed like CH₂O, CO₂ and above 400°C temperature, the thermal fragmentation is formed in which the mass loss occurs due to phenol molecules.

On the above 600°C temperature range, the carbon chare formation occurs and lastly the product remains as residue remains are 1.39 % and 6.25 % on the basis of thermo gravimetric analysis data, the molecular formula of the above polymer monomer is [C₁₄ H₁₆ O₃ Cl₂].½ H₂O.

TG thermogram of poly (4- chlorophenol – methylene- -4- nitrobenzoic acid) in nitrogen atmosphere is shown in Figure.2. From these Figures it is noted that in nitrogen atmosphere, the sample which refluxed at 150°C for 12 hours is more thermally stable than the sample than the sample prepared at 120°C for 6 hours. During product formation the

moisture will be trapped –due to these water molecules the mass loss occurs at around 110-180°C temperature. The degradation temperature is noted in Table 2. After loss of water molecules, the continuous degradation of the pure sample. The most important step is post curing and oxidation degradation in temperature range 180-400°C. The mass loss due to products formed like CH₂O, CO₂ and above 400°C temperature, the thermal fragmentation is formed in which the mass loss occurs due to phenol molecules. On the above 600°C temperature range, the carbon chare formation occurs and lastly the product remains as residue remains are 0.616 % and 10.95 %.

Thermal gravimetric is the method in which the mass of the sample is continuously recorded during heating. The thermo gravimetric curve thus obtained expressing the dependence of the mass change on temperature give information of the sample composition its thermal stability, its thermal decomposition the product form as CH₂O, CO₂, H₂O on heating. This degradation product mass was found to be equivalent to the calculated mass of empirical chemical formula. This may give the correct formula of the given synthesis polymeric unit. During pyrolysis the left residue is corresponds to carbon char residue. The intermediate mass loss is due to loss of low molecular hydrocarbon mass at above 180°C in nitrogen gas. On the basis of TGA data. The polymeric monomer unit molecular formula is [C₁₄H₁₆O₅N₁]._{1/2}

These mass losses have been assigned on the basis of the two aromatic ring with one methylene bridge unit empirical formula of the p- substituted phenol with methylene bridge polymer and the discrepancy may be assigned to the presence of low molecular mass compounds in the sample and its subsequent loss at higher temperature these indices, especially the characteristic temperature, are depends on the rate of heating(rise of temperature) applied during the pyrolysis (normally about 3 °k/min or 5x 10⁻² ks.⁻¹

Table 1: The Infra Red Spectral Data of Phenolic Polymer

Sr. No	Name of the Polymer	Wave Number (cm ⁻¹) of the Band Observed	Probable Assignment
1	Poly(4-Chlorophenol– methylene – 4' – chlorobenzoic acid) (PCPCBA)	3040 2810 1680 1590 1425 1300 675	Broad band due to O-H stretching vibration of phenolic associated-OH group C-H stretching of Ar-CH ₂ group peak due to C=O stretching COOH group of the anionic stretching C-H stretching of -CH ₂ - bridge Due to C-O stretching of phenolic-OH group C-Cl stretching vibration
2	Poly (4- Chlorophenol– methylene -4'- nitrobenzoic acid) (PCPNBA)	3400 3100 1680 1595 1510 1420 1300 1100 710	Broad band due to O-H stretching vibration of phenolic associated-OH group C-H stretching of Ar-CH ₂ group Due to C=O stretching COOH group of the anionic stretching NO ₂ group due to vibration of Ar-NO ₂ C-H bending of- CH ₂ -bridge C-O stretching of phenolic-OH group C-N stretching vibration Due to –C-Cl stretching vibration

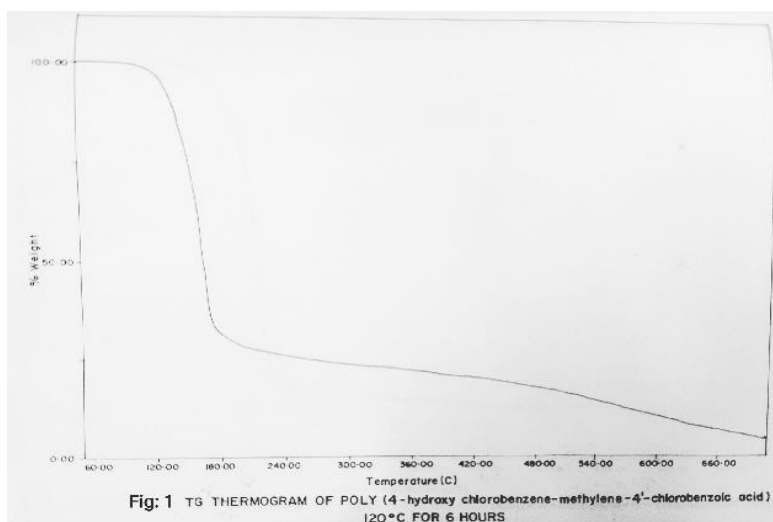


Figure 1: TG thermogram of Poly (4-Hydroxy Chlorobenzene – methylene- -4- Chlorobenzole Acid) 120°C For 6 Hours.

Table 2: Decomposition Pattern and Activation Energy of Phenolic Polymers

Polymer	Sample	Degradation T_d °C	T °C	% mass loss	E_a kJ/mol
1) Poly(4 -chlorophenol -methylene – 4' – chlorobenzoic acid) (PCPCBA)	S1	308	120 400 600	1.09 19.74 14.58	37.14
	S2	308	120 400 600	2.08 86.81	35.00
2) Poly(4 -chlorophenol -methylene - 4' nitrobenzoic acid) (PCPNBA)	S1	328	120 400 800	2.09 64.27 29.87	27.62
	S2	328	120 400 700	2.07 37.51 54.17	28.47

S₁-refluxed on temperature 120°C for 6 hours, S₂-refluxed at 150°C for 12 hours

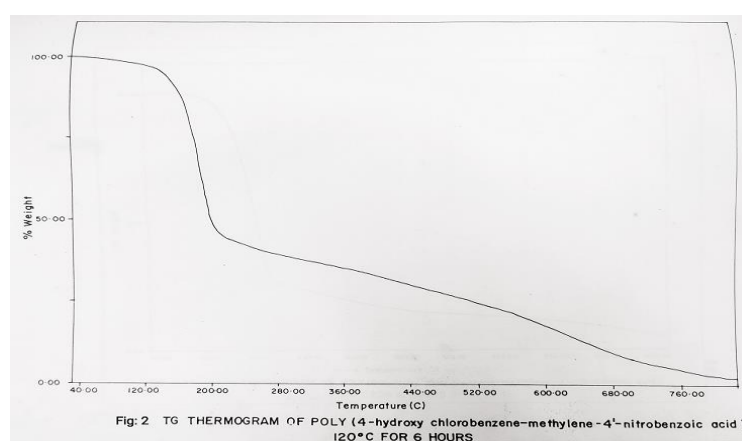


Figure 2: TG Thermogram of Poly (4-Hydroxy Chlorobenzene-4-Nitrobenzoic Acid) 120°C for 6 Hours.

CONCLUSIONS

The result of infra red analysis and thermal gravimetric analysis indicate the more correct formula of monomer unit poly

(4 - chlorophenol – methylene -4 '- nitrobenzoic acid) as $[C_{14}H_{16}O_5N_1]$. And (p'-chlorobenzoic Acid) as $[C_{14}H_{16}O_3Cl_2]$.

The structural unit may be as shown below

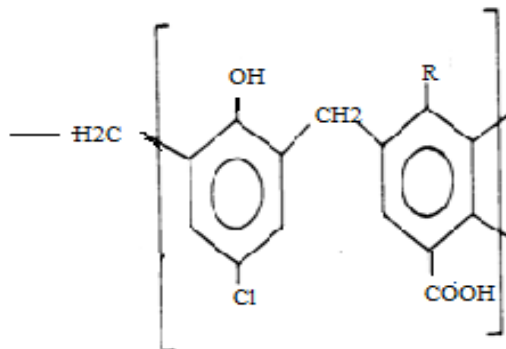


Figure 3

Where,

$R = Cl, NO_2$

Synthesis temperature increase means the molecular weight of the polymer increase in unidirectional chain and gives more thermal stability.

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